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Evaluation of pyrolysis process parameters on polypropylene degradation products

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ABSTRACT

Pyrolysis of polypropylene (PP) with an equilibrium fluid catalytic cracking (FCC) catalyst in a stirred reactor was studied to produce "fuel like" hydrocarbons. The effect of process parameters such as degradation temperature, catalyst/polymer ratio (%), carrier gas type and stirrer rate on the condensed product yield and composition were determined.

Reaction products were determined by GC analysis and shown to contain naphthenes, paraffins, olefins and aromatics.

Temperature was shown to influence PP cracking. The addition of the catalyst has improved the economic viability of the process to produce light hydrocarbons. PP pyrolysis showed the maximum condensed product yields at 450 °C and 10% catalyst respectively. Hydrogen as a reactive carrier gas increased the condensed and paraffinic product yield. The results showed that reactive carrier gases can affect on the product yield and composition patently.

Appropriate heat transfer – by stirring – can increase the catalyst efficiency in a stirred reactor.

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1. Introduction

Plastic is a major component of municipal waste streams in many countries and the waste plastic is bringing about serious environmental problems [1,2]. The main plastics recycled are polyethylene, polyethylene-terepthalate and PP. PP represents 24.3% of United States thermoplastic market and is used in food packaging, medical bags, computer components, automotive industry, pipes and general containers [3].

The versatility of PP is due to its good chemical resistance, mechanical properties, process ability, and its low density.

Thermochemical conversion (via pyrolysis) of waste polymers to low molecular weight compounds is of great interest as an alternative source of energy or chemical raw materials, and can help mitigate environmental issues [4,5]. Pyrolysis is generally defined as the controlled heating of a material in the absence of oxygen [6,7] whereas catalytic pyrolysis can improve the product selectivity and reduce the energy input [8].

The catalytic degradation of polymeric materials has been reported for a range of catalysts centered on active components such as amorphous silica–aluminas, zeolites Y, ZSM-5, acidic catalysts and the new family of MCM materials [9–20]. Even though these catalysts perform well, there use is not feasible due to the cost of manufacturing and the high sensitivity of the process to the cost of the catalyst. An economical improvement of processing the recycling via catalytic cracking would operate in mixing the polymer waste in conjunction with using a fluid catalytic cracking (FCC) system. These FCC catalysts can increase the commercial viability of the conversion of plastic waste co-fed into a refinery FCC unit although the equilibrium FCC catalysts (zeolite based) have better performance in comparison with fresh FCC's in pyrolysis [21–23].

Temperature is likely the most important variable affecting the catalytic cracking of plastics. A review of the literature shows a strong dependence of carbonization products to process parameters such as temperature, catalyst type and polymer/catalyst ratio, heating rate and residence time [11,12,24,25]. However, other process parameters like carrier gas and stirrer rate as function of mass and heat transfer on FCC pyrolysis are limited [11,12].

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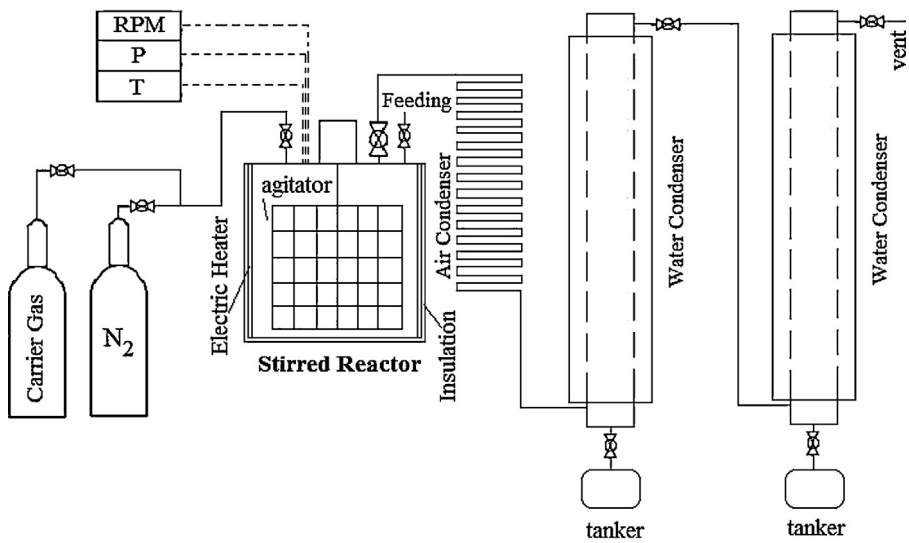

Fig. 1. Flow scheme of the laboratory stirred reactor.

Liquefaction of waste plastics research has involved the use of high temperature and pressure reactors in the presence of hydrogen, or a hydrogen donor such as tetralin or oil and/or the presence of catalysts [26].

Stirring of the polymer melt greatly accelerates the heat transfer process and result in energy savings and temperature homogeneity. Discontinuous (batch process) and continuous (alternating batch or cascade) stirred reactors are generally used in commercial-scale melt phase pyrolysis plants. These units are relatively simple, basically consisting of a large stainless steel vessel with indirect heating, a large stirrer and possibly internals such as baffles to enhance mixing and heat exchanger surfaces [27].

The aim of this study is to investigate the effects of (i) temperature, (ii) catalyst/PP ratio, (iii) carrier gas, and (iv) stirrer rate on PP FCC pyrolysis on the products yield and condensed product composition. GC analysis was used to determine product composition.

2. Experimental

2.1. Material

PP (PI080 grade, Bandar Imam Petrochemical Co., Mahshahr, Iran), ethylene and propylene (purity 99.9%, Tehran Petrochemical Co, Tehran, Iran), and N_2, Ar, H_2 and He gases (purity 99.99%, Roham Co. Tehran, Iran) were used as received. The equilibrium FCC catalyst (zeolite based, Abadan FCC Refinery) was regenerated at 750 °C with mild steaming and its composition/properties are: Surface Area (BET) 235 m^2/g, SiO_2 80.10%, Al_2O_3 13.40%, Na 0.30%, Ca 1.54%, Fe 0.20%, V(ppm) 450, Ni(ppm) 180 and Si/Al is 6.

2.2. Instruments

2.2.1. Pyrolysis process

Pyrolysis experiments were carried out in a 1 L stirred semi-batch reactor (buchi pilot plant with a custom built reactor) under atmospheric pressure and the schematic diagram is shown in Fig. 1. The fixed experimental conditions are as follows: PP (100 g), FCC catalyst and carrier gas stream (300 mL min^{-1}), heating rate (25 °C min^{-1}) up to the final temperature. The non-condensable products were vented after cooling through three condensers. The condensed hydrocarbons products were stored in glass sampling bottles. The components of total condensed hydrocarbons (residue in the condensers contained C3–C15) were quantified by gas chromatography (GC). The non-condensable products were not analyzed. The solid char yield was determined gravimetrically after completion of the reaction. The non-condensable yield was calculated by subtracting the weight of the condensed hydrocarbons and solid products from the sample weight.

2.2.2. Analyzer instruments

GC analyses were performed on a Varian CP-3800 GC fitted with a flame ionization detector (at 280 °C) and Varian CP-8200 auto sampler. Separation was achieved using a VF-5 ms capillary column ((30 m × 0.25 mm I.D, Varian) with a temperature program of 200 °C (4 min) then heated to 280 °C (7 min) at a rate of 10 °C min^{-1} and He as the carrier gas (1.0 mL min^{-1}). The identity of compounds was confirmed with known standards, special software and expert GC man.

3. Results and discussion

Mass balance of PP pyrolysis products (condensable products, solid residue and noncondensable by difference) were determined

Table 1
The effect of temperature on the products yield and the condensed product composition.

Pyrolysis temperature (°C)	Condensed product yield (%)	Non-condensable product yield (%)	Coke yield (%)	Olefins (%)	Paraffins (%)	Naphtenes (%)	Aromatics (%)	Olefin/paraffin ratio
420	88.6	8.3	3.1	43.65	35.45	17.43	3.47	1.23
450	92.3	4.1	3.6	44.63	32.87	17.23	5.27	1.36
480	82.4	12.5	5.1	46.34	29.77	16.34	7.55	1.56
510	76.1	17.1	6.8	48.23	27.65	13.37	10.75	1.74

Catalyst/PP = 0.1, stirrer rate: 50 r * min^{-1}, carrier gas: N_2.

Table 2
The effect of temperature on the carbon number distribution of the condensed product composition.

Type	Temperature			
	420 °C	450 °C	480 °C	510 °C
C3 (%)	0.744	0.988	1.302	1.982
C4 (%)	8.034	8.331	8.73	10.763
C5 (%)	15.498	16.45	17.681	18.647
C6 (%)	15.298	15.498	15.692	15.893
C7 (%)	17.149	18.684	20.913	21.076
C8 (%)	14.244	13.718	13.525	12.765
C9 (%)	14.302	13.547	12.197	11.235
C10 (%)	7.345	6.959	6.336	5.067
C11 (%)	4.066	3.309	2.197	1.786
C12 (%)	2.776	2.116	1.119	0.654
C13 (%)	0.455	0.356	0.276	0.12
C14 (%)	0.089	0.044	0.032	0.012
Sum (C5–C9) (%)	76.491	77.897	80.01	79.616
Ave. molecular weight (g mol^{-1})	101.86	99.85	97.08	93.92

Catalyst/PP = 0.1, stirrer rate: 50 r * min^{-1}, carrier gas: N_2.

Table 4
The effect of catalyst/PP ratio on the carbon number distribution of the condensed product composition.

Type	Catalyst/PP ratio			
	0.10	0.20	0.40	0.60
C3 (%)	0.988	1.114	1.298	1.324
C4 (%)	8.331	10.529	10.842	10.897
C5 (%)	16.45	19.038	19.876	20.087
C6 (%)	15.5	17.408	18.342	18.563
C7 (%)	18.68	22.014	22.725	22.193
C8 (%)	13.72	12.437	12.563	12.349
C9 (%)	13.55	10.551	10.021	10.894
C10 (%)	6.955	4.304	2.776	2.332
C11 (%)	3.31	1.731	1.021	1.054
C12 (%)	2.116	0.78	0.503	0.271
C13 (%)	0.356	0.076	0.021	0.027
C14 (%)	0.044	0.018	0.012	0.009
Sum (C5–C9) (%)	77.899	81.448	83.527	84.086
Ave. molecular weight (g mol^{-1})	99.85	93.69	91.69	91.46

T: 450 °C, stirrer rate: 50 r * min^{-1}, carrier gas: N_2.

gravimetrically (Tables 1–8) for the reactor variables of temperature (420–510 °C), FCC catalyst/PP ratio (0–60%), stirrer rate (0–300 r * min^{-1}) and carrier gas (N_2, H_2, He, Ar, ethylene and propylene).

3.1. Effect of the degradation temperature

The effect of temperature on the catalytic pyrolysis of PP was examined and the product yields (condensed, non-condensable and coke) are given in Table 1. The main product fraction was condensed hydrocarbons (yields up to 92.3%). As the pyrolysis temperature increased the coke yield also increased. At 510 °C, the coke content was 6.8%, although the condensed hydrocarbons shows a maximum yield at 450 °C and non-condensable products reached a minimum content also at 450 °C. Jung et al. [15] have seen a decrease in pyrolytic liquid with temperature increasing in 668–746 °C range although it is interesting to notice that some reports have showed a peak in liquid yield with temperature increasing [11,12].

The condensable products were characterized by GC and composition as a function of temperature is given in Tables 1 and 2. These reaction products were grouped into different classes, i.e., naphthenes (cycloalkanes), paraffins (alkanes), olefins (alkenes) and aromatics (Table 1). The results show that aromatic products and olefin to paraffin ratio increased with increasing temperature. The distribution of C3–C14 condensed hydrocarbon products and average molecular weights with pyrolysis temperature are given in Table 2.

At 420 °C, PP is converted to condensed products dominated by aliphatic hydrocarbons (olefins at 43.65% and paraffins at 35.45%) with minor amounts of aromatics (3.47%) and naphthenes (17.43%). For light fuels, the C5–C9 fraction is desirable for a gasoline feedstock. The C5–C9 fraction was shown to be the major product (76.49%) in the condensed product.

At 450 °C, the condensed product was composed of olefins (44.63%), paraffins (32.87%), and aromatics (5.27%) while at 480 °C, the olefin (46.34%) and paraffin (29.77%) compounds were enhanced to be the main components in the condensed product. It clearly shows that the reduction in naphthene and paraffin yields was in favor of double bond formation indicating that unsaturation, cyclization and aromatization took place around 480 °C. While at 510 °C, the condensed hydrocarbons decreased by about 16.2% and reached a yield of 76.1%. The highest amount of gaseous products was obtained at 510 °C with yield of 17.1%. The C5–C9 fraction was the main compounds like the other pyrolysis processes at different temperatures.

The results show that the product molecular weight decreases with temperature. The predominant processes at higher temperatures involve the conversion of liquid products directly to aromatics and some gases, and the stripping of gases to form aromatics and finally char. The formation of aromatics in the pyrolysis of polyolefin is accomplished using the Diels–Alder reaction, followed by dehydrogenation. The detailed mechanism of the formation of benzene–toluene–xylene (BTX) aromatics is presented in some papers [29,30].

The results show that the carbon number distribution of the products shifts to lower carbons with the temperature increases from 420 to 510 °C and the gasoline – C5–C9 – yield shows a weak peak at 480 °C although Lin et al. [25] showed a decrease in gasoline range with temperature increasing in a gas phase reactor. On the other hand Cardona et al. [31] reported the same molecular weight distribution of the product in a stirred reactor.

3.2. Effect of the FCC catalyst content

The effect of increasing the catalyst/PP ratio from 0.1 to 0.6 on the condensable, non-condensable and coke product yields are given in Table 3. The maximum condensed product yield was

Table 3
The effect of catalyst/PP ration on the products yield and the condensed product composition.

Catalyst/PP ratio	Condensed product yield (%)	Non-condensable product yield (%)	Coke yield (%)	Olefins (%)	Paraffins (%)	Naphtenes (%)	Aromatics (%)	Olefin/paraffin ratio
0	95.2	4.4	0.4	n.d.*	n.d.	n.d.	n.d.	n.d.
0.1	92.3	4.1	3.6	44.63	32.87	17.23	5.27	1.36
0.2	85.2	9.6	5.2	46.57	29.36	17.28	6.79	1.59
0.4	79.3	13.8	6.9	48.04	24.77	18.34	8.85	1.94
0.6	76.7	14	9.3	50.08	23.35	16.6	9.97	2.14

T: 450 °C, stirrer rate: 50 r * min^{-1}, carrier gas: N_2.
* Not determined.

Table 5
The effect of carrier gas on the product yield and the condensed products composition.

Carrier gas	Molecular weight	Condensed product yield (%)	Non condensable product yield (%)	Coke yield (%)	Olefins (%)	Paraffins (%)	Naphtenes (%)	Aromatics (%)	Olefin/paraffin ratio
H_2	2	96.7	3	0.3	30.86	46.53	20.54	2.07	0.66
He	4	94.7	3.2	2.1	43.32	33.41	19.29	3.98	1.3
N_2	28	92.3	4.1	3.6	44.63	32.87	17.23	5.27	1.36
Ethylene	28	93.8	5.1	1.1	41.76	34.76	19.75	3.73	1.2
Propylene	42	87.8	9.7	2.5	42.36	31.85	20.92	4.87	1.33
Ar	37	84.8	9.8	5.4	45.21	25.27	21.93	7.59	1.78
No carrier gas	51.3	33.8	14.9	n.d.*	n.d.	n.d.	n.d.	n.d.	n.d.

T: 450 °C, stirrer rate: 50 r * min^{-1}, catalyst/PP = 0.1.
* Not determined.

achieved with a 10% FCC catalyst. However, pyrolysis without catalyst showed a maximum condensed yield comprising of waxes (>90%) which was not suitable for fuel. The pyrolysis of PP in a gas phase reactor with only 2% FCC catalyst content can change the product composition and produce the low molecular weights without wax and vaseline [25]. Generally, the high surface area catalysts can change the nature of the pyrolysis and affect on the results even in low contents [32,33]. The results show that the non-condensable and coke yields increase with catalyst content.

The coke yield may be attributable to aromatization and dehydrogenation on the catalyst surface. The composition of paraffins, naphthenes, olefins and aromatics in the condensed fraction, as a function of catalyst content are given in Table 4. The results show that the main components were olefins (44–50%) and paraffins (23–33%), with minor amounts of aromatic (<10%) and naphthenes (17.23–18.34%). These data indicate that dehydrogenation increases moderately with catalyst content as judged by the aromatics product and olefin/paraffin ratio. The product carbon number distribution and molecular weight of the condensed hydrocarbons at differing catalyst ratios are given in Table 4. The results show that as the catalyst ratio increases the product molecular weight slightly decreases. Furthermore, as the catalyst/polymer ratio increases the molecular size selectively and the gasoline product (C5–C9) slightly increases (Table 4).

The results obtained in this section are in agreement with the literature [11,12]. This suggests that the degradation of high molecular weight olefinic molecules occurs over the catalyst surface forming smaller and selected molecules within the pores of the zeolites for further cracking and product selectivity [34].

The results show that the condensed hydrocarbons are distributed from C3 to C13 compounds although the catalyst increasing tends to show a condensed product with narrower carbon number distribution. C5–C9 in the condensed product are the main compounds.

3.3. Effect of carrier gas

The influence of carrier gas (H_2, N_2, He, Ar, ethylene, propylene and no gas) used in the pyrolysis of PP was examined and the product yields (condensed, non-condensable and coke) are given in Table 5. In H_2, the condensed product yield was 96.7%. In contrast, with no carrier gas the condensed product yield of 51.3% was the lowest. These results are in accord with Williams and Slaney [26] and previous works on the LLDPE and HDPE pyrolysis [11,12].

Reactivity is specially defined in this work as the ability of the carrier gas to take part in the pyrolysis process. The inert carrier gas does not take part in the pyrolysis process but is only involved in transportation of the vaporized products. The pyrolysis results show that molecular size of the carrier gas aids in conveying of the products and is temperature dependent. The flow rate is equal for all of carrier gases but before reactor arrival; in the reactor low molecular weights show more activity with temperature increasing and it can help the products to leave the reactor easily. In same condition, the more residence time in the reactor increases the second reaction like dehydrogenation and more cracking take part in the products. Consequently in the neutral carrier gas, helium with lower molecular weight, gave a lower olefin/paraffin ratio, olefin and aromatic components in comparison with Ar and N_2.

Hydrogen, ethylene and propylene are good examples of reactive carrier gases, although H_2 has more reactivity in comparison with the others. Hydrogen can protect the pyrolysis products, by hydrogenation, and increase liquid yields. The results show that the reactivity of the carrier gas can affect on the coke formation (Table 5). The reactive carrier gases decrease the coke yield by reducing aromatization and dehydrogenation. The coke yields obtained were of 0.3% and 14.9% respectively for H_2 and no-gas.

Table 5 shows the variation of the condensed hydrocarbons composition with respect to different carrier gases too. The results show that paraffin content increased using H_2, ethylene and

Table 6
The effect of carrier gas on the carbon number distribution of the condensed product composition.

Type	Carrier gas					
	N_2	He	Ar	Ethylene	Propylene	H_2
C3	0.988	1.034	0.782	1.362	1.098	1.434
C4	8.331	9.459	8.643	10.567	9.987	8.904
C5	16.45	16.872	15.324	18.754	17.493	17.936
C6	15.498	17.381	16.345	14.411	16.584	18.694
C7	18.684	19.398	15.764	21.379	19.639	18.784
C8	13.718	14.62	14.234	12.443	13.593	15.426
C9	13.547	13.046	11.476	12.614	10.137	12.056
C10	6.959	4.283	7.392	5.257	7.305	3.976
C11	3.309	2.298	5.375	1.935	2.503	1.886
C12	2.116	1.326	3.871	1.079	1.229	0.763
C13	0.356	0.249	0.645	0.178	0.346	0.124
C14	0.044	0.034	0.149	0.021	0.086	0.017
Sum (C5–C9)	77.897	81.317	73.143	79.601	77.446	82.896
Ave. molecular weight	99.85	96.65	102.39	95.42	96.76	95.11

T: 450 °C, stirrer rate: 50 r * min^{-1}, catalyst/PP = 0.1.

Table 7
The effect of stirrer rate on the products yield and the condensed product composition.

Agitator rate (r * min^{-1})	Condensed product yield (%)	Non-condensable product yield (%)	Coke yield (%)	Olefins (%)	Paraffins (%)	Naphtenes (%)	Aromatics (%)	Olefin/paraffin ratio
0-without stirrer-	65.3	26.5	8.2	n.d.*	n.d.	n.d.	n.d.	n.d.
0	81.6	13.5	4.9	46.87	29.43	19.17	4.53	1.59
50	92.3	4.1	3.6	44.63	32.87	17.23	5.27	1.36
100	87.4	9.5	3.1	40.376	30.741	20.986	7.897	1.31
300	82.4	14.6	3	39.763	30.596	19.94	9.701	1.29

T: 450 °C, catalyst/PP = 0.1, carrier gas: N_2.
* Not determined.

Table 8
The effect of stirrer rate on the carbon number distribution of the condensed product composition.

Type	Agitator rate (r * min^{-1})			
	0	50	100	300
C3	1.367	0.988	0.327	1.087
C4	7.261	8.331	5.794	5.197
C5	14.362	16.45	15.215	14.943
C6	14.864	15.498	12.315	15.342
C7	19.237	18.684	24.936	22.933
C8	12.385	13.718	15.034	12.557
C9	14.343	13.547	16.036	15.46
C10	7.596	6.959	6.628	6.486
C11	4.728	3.309	2.417	4.043
C12	2.869	2.116	1.115	1.602
C13	0.818	0.356	0.172	0.33
C14	0.17	0.044	0.011	0.02
Sum (C5–C9)	75.191	77.897	83.536	81.235
Ave. molecular weight	102.89	99.85	101.53	101.78

T: 450 °C, catalyst/PP = 0.1, carrier gas: N_2.

propylene, while the aromatic products decreased. The C3–C14 distribution and average molecular weight of condensed hydrocarbons for each of the carrier gases are given in Table 6. It appears that the condensed hydrocarbons distribution shifted to lower molecular weight with a higher proportion in the gasoline range with decreasing carrier gas molecular weight as well as an increase of the reactivity. Higher molecular weight carrier gases gave a little broader carbon number distribution although the C4–C9 fraction in all of these atmospheres was the main products.

In comparison with the neutral carrier gases of similar molecular weight, the reactive carrier gases improved the product formation. This is due to the reactive gases can shift the equilibrium to generate a greater liquid yield [11,12]. H_2, ethylene and propylene can take part in the pyrolysis process at high temperatures by radical production. H_2, ethylene and propylene can produce the radical in the high temperature easily and the radicals can take part in the pyrolysis process through the radical formation and its contribution in the process is affected by carrier gas type, process temperature and catalyst type and ratio.

3.4. Effect of stirrer rate

Table 7 shows the yield of the PP pyrolysis products with reactor stirrer rate. At 50 r * min^{-1} the maximum condensed hydrocarbon yield was obtained though the reactor with and without stirrer show obvious difference between the results. The reactor without stirrer presence shows very weak radiation heat transfer in high temperatures and poor thermal conductivity of the polymer increase the residence time of the pyrolysis process. More residence time, non-homogeneity of polymer/catalyst mixture and temperature gradient change the product obviously.

Within the reactor containing a high viscosity melt, a temperature gradient from heated wall to the center will be observed. Therefore, attention to reactor and stirrer design as well as speed need to be considered to obtain uniform reaction temperature since this will affect product yield and composition.

Appropriate or inadequate heat transfer can affect on the pyrolysis of PP and molecular weight distribution of the products. Poor heat transfer can decrease the catalyst efficiency patently and increase the undesirable products such as char and gaseous products [11,12,33,35].

The composition of condensed hydrocarbons with reaction stirrer speed is given in Table 7 too.

In high temperatures and the progress of pyrolysis reaction, the viscosity decrease obviously and it can change the trend of heat and mass transfer of laminar to tubular and it maybe increase the temperature distribution. The temperature distribution increases the high and low temperature areas and the high temperatures can intensify the Diels–Alder mechanism and increase the aromatics content.

Table 8 shows that stirrer rate has no obvious effect on the molecular weight of condensed hydrocarbons although gasoline range components peak at 100 r* min^{-1}. The results show that condensed hydrocarbons are distributed from C3 to C13 compounds and C5–C9 were the main products.

4. Conclusion

Catalytic pyrolysis of PP was successfully achieved in a stirred laboratory reactor. The catalytic degradation of PP generated compounds in the C3–C14 range of which the C5–C9 were of most interest for use as a liquid fuel substrate. Observed differences in product yields and product distributions can be influenced by reaction conditions, most notably: temperature, catalyst level, carrier gas and stirrer speed. Hydrogen resulted in improved product yield by stabilizing the products. These results can be directly applied to design a pilot scale system for waste plastic utilization to produce liquid fuels. The results showed that the construction of pyrolysis plant beside the olefinic petrochemical plants and the use of olefin plant emissions can produce the superior pyrolitic products. Totally consideration of carrier gas type and agitator type and speed besides temperature and catalyst type and ratio can produce the desired products.

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